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STENCHES FOR DETECTING LEAKAGE OF BLUE WATER GAS AND NATURAL GAS

BY

S. H. KATZ AND V. C. ALLISON



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STENCHES FOR DETECTING LEAKAGE OF BLUE WATER GAS AND NATURAL GAS.

BY S. H. KATZ AND V. C. ALLISON.

INTRODUCTION.

This paper is published by the Bureau of Mines in response to requests for more information on the use of stenchers as warnings in mines or other places, and especially on the costs of stenchers and the names of dealers. Thus the information given is supplementary to that contained in Technical Paper 244.¹

Loss of life and property often result from leakage in the distribution of natural gas and blue water gas used for fuel and illumination. The detection of leaks by adding stenchers to the gas would reduce losses materially and would therefore promote economy to the producer and safety to the consumer.

Blue water gas is particularly dangerous, as it is almost odorless and is very poisonous because of its large content, nearly 35 per cent, of carbon monoxide. The addition of a stench to the gas, which certain German cities require by law,² gives warning of the presence of the gas and makes possible the saving of life.

Natural gas also has little odor. Leaks in the pipes, particularly out of doors, are seldom detected until the loss of gas is noticed, and then the leaks are difficult to find. Many gas explosions, some of which wreck buildings, might be prevented by a warning stench. Moreover, although the principal need for stenchers is in natural and blue water gas, they might also be used profitably to strengthen the odor of other gases.

ACKNOWLEDGMENTS.

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¹ Katz, S. H., Allison, V. C., and Egy, W. L. Use of stenchers as a warning in mines: Tech. Paper 244, Bureau of Mines, 1919, 31 pp. 1 pl., 4 figs.

Allison, V. C., and Katz, S. H., An investigation of stenchers and odors for industrial purposes: Jour. Ind. and Eng. Chem., vol. 11, 1919, pp. 336-338.

² Palmer, C. S., Producer gas, its manufacture and use: Proc. Eng. Soc. Western Pennsylvania, vol. 34, 1918-1919, pp. 331-363; statement on p. 357.

York City; W. H. Fulweiler, chief chemist United Gas Improvement Co., Philadelphia, Pa.; and to W. W. Odell, gas engineer, Urbana experiment station, Bureau of Mines.

PROPERTIES OF STENCHES.

Table 1 gives some of the chemical, physical, and physiological properties of the stenchcs that have been investigated. Another requisite of the materials besides the properties listed is that they must not cause deterioration of the metal pipes, rubber gaskets, or of the leather used in meters. For this reason butyric or valeric acid should not be used.

TABLE 1.—*Chemical, physical, and physiological properties of chemicals used as stench.*

Name.	Chemical formula.	Molecular weight.	Specific gravity.	Boiling point.	Freezing point.	Solubility in water.			Character of odor.	Physiological properties of vapor.
						Grams per 100 grams water.	Temperature.	Chemical action.		
Amyl acetate.....	$\text{CH}_3\text{COO}(\text{CH}_2)_4\text{CH}_3$	130.2	0.875	148	-175	0.2	20	Slow hydrolysis.....	Banana oil. ¹	Harmless.
Ethyl acetate.....	$\text{CH}_3\text{COO.C}_2\text{H}_5$	88.1	.900	77.4	-83.8	8.33	20	do.....	Fruity, pleasant.....	Do.
Amyl alcohol.....	$\text{CH}_3(\text{CH}_2)_4\text{OH}$	88.1	.817	137.8	—	2.67	22	None.....	Alcoholic.....	Do.
Butyric acid.....	$\text{CH}_3(\text{CH}_2)_3\text{COOH}$	88.1	.960	162.3	-7.9	Soluble in all proportions.		do.....	Very disagreeable.....	Do.
Valeric acid.....	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	102.1	.942	186.4	-58.5	3.5	16	do.....	do.....	Do.
Ethyl ether.....	$\text{C}_2\text{H}_5_2\text{O}$	74.1	.719	35	-112.6	6.95	20	Probably slow hydrolysis.	Pungent.....	Soporific.
Phenyl isocyanide.....	$\text{C}_6\text{H}_5\text{.NC}$	103.1	.977	195				Probably very slight.	Very disagreeable.....	Unknown.
Allyl isothiocyanate.....	$\text{CH}_2\text{.CH.CH}_2\text{.NCS}$	99.1	1.017	151		Very slightly soluble.		do.....	Mustard oil, disagreeable.	Lachrymatory and toxic.
Methyl isothiocyanate.....	$\text{CH}_3\text{.NCS}$	73.1	1.069	119	34	Probably slightly soluble.		do.....	do.....	Do.
Amyl isovalerate.....	$\text{C}_5\text{H}_{11}\text{.COO.C}_4\text{H}_9$	172.2	.855	190				Slow hydrolysis.....	Very disagreeable.....	Harmless.
Butyl mercaptan.....	$\text{CH}_3(\text{CH}_2)_3\text{SH}$	90.2	.858	97		Insoluble.		Stable.....	do.....	Do.
Isobutyl mercaptan.....	$(\text{CH}_3)_2\text{CH.CH}_2\text{SH}$	90.2	.88	88		Probably insoluble.		do.....	do.....	Unknown. ³
Ethyl mercaptan.....	$\text{CH}_3\text{CH}_2\text{SH}$	62.1	.838	37	-144.4	1.5		do.....	do.....	Harmless.
Propyl mercaptan.....	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$	76.1	.838	67		Very slightly soluble.		do.....	do.....	Unknown. ³
Methyl salicylate.....	$\text{HO.C}_6\text{H}_4\text{.COO.CH}_3$	152.1	1.186	222.2	-8.3	.074	20	Slow hydrolysis.....	Oil of wintergreen, pleasant.	Harmless.
Amyl thioether.....	$(\text{C}_5\text{H}_{11})_2\text{S}$	174.2		216		Insoluble.		Stable.....	Very disagreeable.....	Unknown. ³
Ethyl thioether.....	$(\text{C}_2\text{H}_5)_2\text{S}$	90.2	.837	92	-99.5	.313	20	None.....	do.....	Do. ³
Carbon tetrachloride.....	CCl_4	153.8	1.584	76.74	-19.5	.080	20	do.....	Sweet, unpleasant.....	Soporific.
Chloroform.....	CHCl_3	119.4	1.499	62	-63.2	.822	20	do.....	Sweet, agreeable.....	Do.
Iodoform.....	CHI_3	393.8		119		.0106	25	do.....	Unpleasant.....	Harmless.
Artificial musk.....			1.08			.19	20	None.....	Pleasant.....	Do. ³
Nitrobenzene.....	$\text{C}_6\text{H}_5\text{.NO}_2$	123.1	1.199	208.4	5.71			Stable.....	Almonds, pleasant.....	Toxic.
Oil of pepper mint.....			.905	115.2	-42	Soluble in all proportions.		None.....	Very disagreeable.....	Harmless.
Pyridine.....	$\text{C}_5\text{H}_5\text{N}$	79.1	.960							Toxic.

¹ Thick.
² Pleasant to most people, disagreeable to some.
³ Probably harmless.
⁴ Decomposes.
⁵ Unpleasant in higher concentrations.

Not all of the stenchcs in Table 1 are suitable for use in gas lines, but for the sake of comparison all that were investigated are tabulated. Of the chemicals listed only the following are desirable for use in city gas: Allyl isothiocyanate, amyl isovalerate, amyl thioether, butyl mercaptan, ethyl mercaptan, ethyl thioether, isobutyl mercaptan, methyl isothiocyanate, phenyl isocyanide, propyl mercaptan, and pyridine. Each of these substances has a disagreeable odor, which is necessary. The properties of individual stenchcs are discussed in detail on page 7.

INTENSITIES OF STENCHES.*

APPARATUS FOR MEASURING INTENSITIES OF STENCHES.

The apparatus ("odorometer") used in measuring the intensity of stenchcs is shown in figure 1. A number of Venturi meters were so arranged that a measured volume of air could pass at a uniform rate through or over the chemical tested; this air could then be mixed with another measured volume of pure air also flowing at a uniform rate. The concentration of the chemical in the air was measured by determining its loss in weight after a measured volume of air had passed through or over it. From this loss in weight and the total volume of air with which the chemical was mixed, the concentration in milligrams per liter of air, and in parts of vapor per million parts of air was determined.

From the vessel containing the chemical the mixture of air and chemical passed through a rubber tube with a glass funnel at the open end. The operator placed this funnel over his nose to prevent the issuing mixture from being contaminated by the air in the room. It is possible, of course, that the addition of natural gas or blue water gas would change somewhat the recorded results.

The apparatus was placed in a hood, and the room was well ventilated to protect the operator from the effects of smelling the chemical.

In the scale of intensities five degrees were adopted, as follows: 1, detectable; 2, faint; 3, easily noticeable; 4, strong; 5, very strong. The rating of the concentration of any chemical depended, of course, on the sensibility and judgment of the observer. On known concentrations of the stench in air the tests were made with a single inhalation of the gas mixture as it escaped from the funnel held over the nose. Concentrations found by the funnel method are much larger than those likely to be found by similar observations made in an atmosphere of stench that completely surrounds the observer and in which many inhalations may be taken; with a number of inhalations the perception of the odor may increase, although the olfactory nerves eventually lose sensibility to the odor of some stenchcs, as usually occurs on prolonged exposure to the odors of a slaughter-

* Allison, V. C. and Katz, S. H., An investigation of stenchcs and odors for industrial purposes: Jour. Ind. Eng. Chem., vol. 11, No. 4, 1919, pp. 336-338.

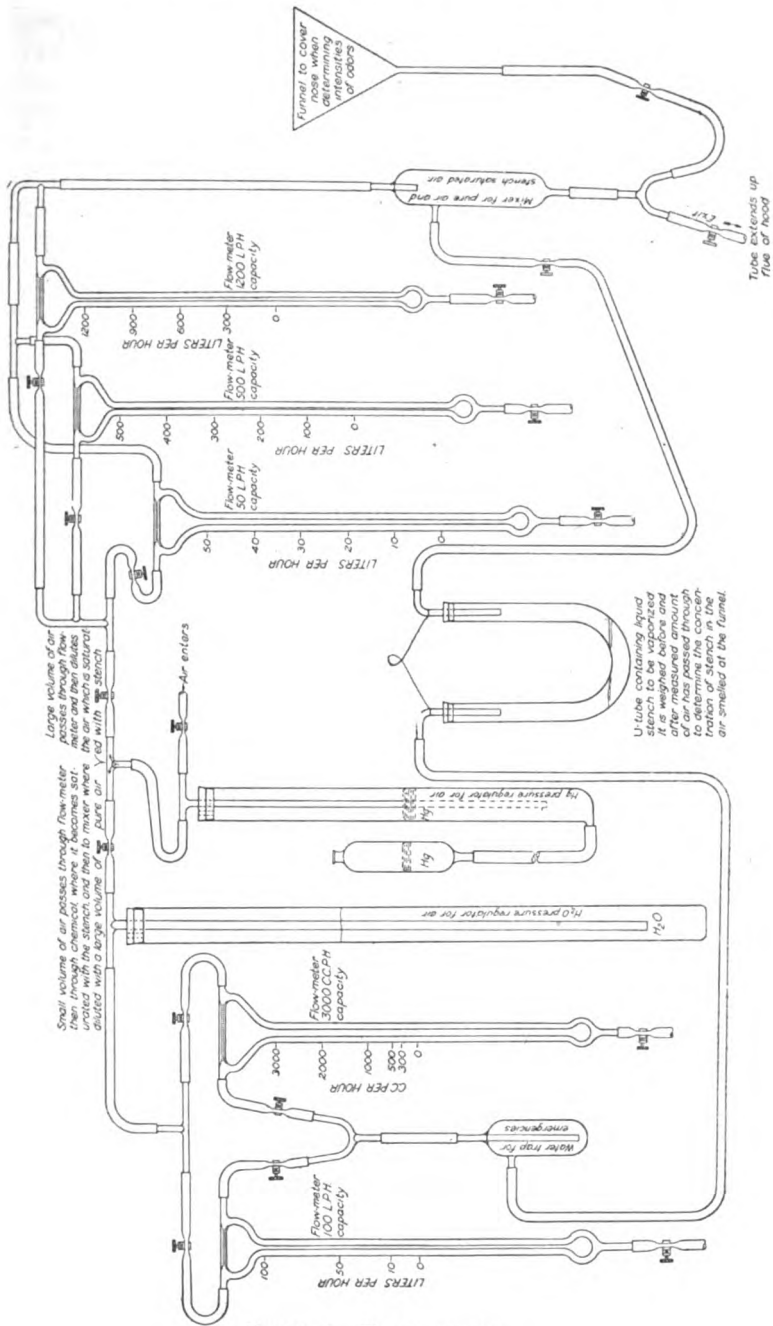


FIGURE 1.—The odorometer.

house. Only the first impression, however, is important in these tests for warning odors.

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TABLE 2.—Results of measurement of the intensity of various stenches.

Chemical.	Volumes of the chemical, as a perfect gas, per million volumes of air.					Milligrams of chemical per cubic foot of air.					Milligrams of chemical per liter of air.				
	Detect- able.	Faint.	Easily notice- able.	Strong.	Very strong.	Detect- able.	Faint.	Easily notice- able.	Strong.	Very strong.	Detect- able.	Faint.	Easily notice- able.	Strong.	Very strong.
Allyl isothiocyanate.....	2	3	6	8	50	0.2	0.3	0.7	0.9	6	0.008	0.012	0.024	0.030	0.201
Amyl acetate.....	7	10	13	90	246	1.1	1.5	2	14	38	.039	.053	.067	.478	1.326
Amyl alcohol.....	63	83	123	439	601	6.4	8.5	13	46	61	.225	.290	.442	1.581	2.167
Amyl isovalerate.....	1.7	3	6	10	12	.4	.5	1	2	2.3	.012	.018	.039	.072	.082
Amyl thioether.....	.2	1	1.6	1.7	2.2	.04	.2	.3	.4	.5	.001	.007	.0115	.012	.015
Artificial musk.....	2.4	6	18	91	161	1.001	.6	2	9	16	1.0004	.021	.042	.039	.580
Butyric acid.....	6	12	18	38	56	.5	1.0	2	3	5	.009	.027	.055	.130	.177
Butyl mercaptan.....	718	1,461	1,588	4,964	6,091	128	260	283	886	1,087	4.333	9.222	10.024	31.333	38.144
Carbon tetrachloride.....	674	1,389	2,000	5,887	9,528	93	192	360	816	1,321	3.300	6.800	12.733	28.833	46.666
Chloroform.....	190	339	615	1,286	1,753	19.4	34.6	63	126	191	.686	1.224	2.219	4.457	6.733
Ethyl acetate.....	1,923	3,352	4,927	5,825	19,982	165.1	287.7	423	500	1,715	5.853	10.167	14.944	17.067	60.600
Ethyl ether.....	18	35	73	141	198	1.3	2.5	5	10	14	.046	.088	.186	.357	.501
Ethyl mercaptan.....	3	12	29	61	74	.3	1.2	3	6	8	.012	.042	.107	.223	.271
Ethyl thioether.....	1.1	5	7	11	16	1.5	.5	.7	1	2	.018	.018	.025	.041	.060
Iodoform.....	3.5	13	23	36	48	.4	1.1	2	3	4	.008	.039	.067	.108	.144
Isobutyl mercaptan.....	5	23	29	124	244	2.8	4	5	16	42	.100	.145	.179	1.526	.144
Methyl isothiocyanate.....	16.1	29	36	114	296	4	5	6	16	9.9	.146	.178	.222	.563	.493
Methyl isobutylate.....	29	36	44	114	296	4	5	6	16	9.9	.032	.032	.109	.332	.348
Nitrobenzene.....	29	36	44	114	296	4	5	6	16	9.9	.032	.032	.109	.332	.348
Oil of peppermint.....	5	1	3	10	25	.06	.1	.4	1	3	.002	.005	.013	.042	.105
Phenyl isocyanide.....	2	7	9	14	17	.2	.6	.8	1.2	1.6	.006	.020	.028	.043	.054
Propyl mercaptan.....	10	45	93	700	1,764	.9	4	9	64	162	.032	.146	.265	2.265	5.710
Pyridine.....	7	29	125	332	962	.8	3.4	1.5	39	114	.029	.119	.523	1.394	4.086
Valeric acid.....	7	29	125	332	962	.8	3.4	1.5	39	114	.029	.119	.523	1.394	4.086

1 Maximum concentration obtainable.

RESULTS OF MEASUREMENTS.

The results of the measurements that were made with one inhalation are given in Table 2 and expressed graphically in figure 2. Wide difference in the concentrations of the various stenches that produce a definite intensity of odor appear.

Those substances that have a soporific effect when inhaled require the greatest concentrations to give a definite intensity of odors, probably because of their anæsthetizing action on the olfactory nerves. Such substances would be of least value for use as stenches. Amyl thioether gave the highest odor intensities with the smallest concentrations of any of the liquid substances tested; only 0.4 milligram per cubic foot was needed to produce strong intensity.

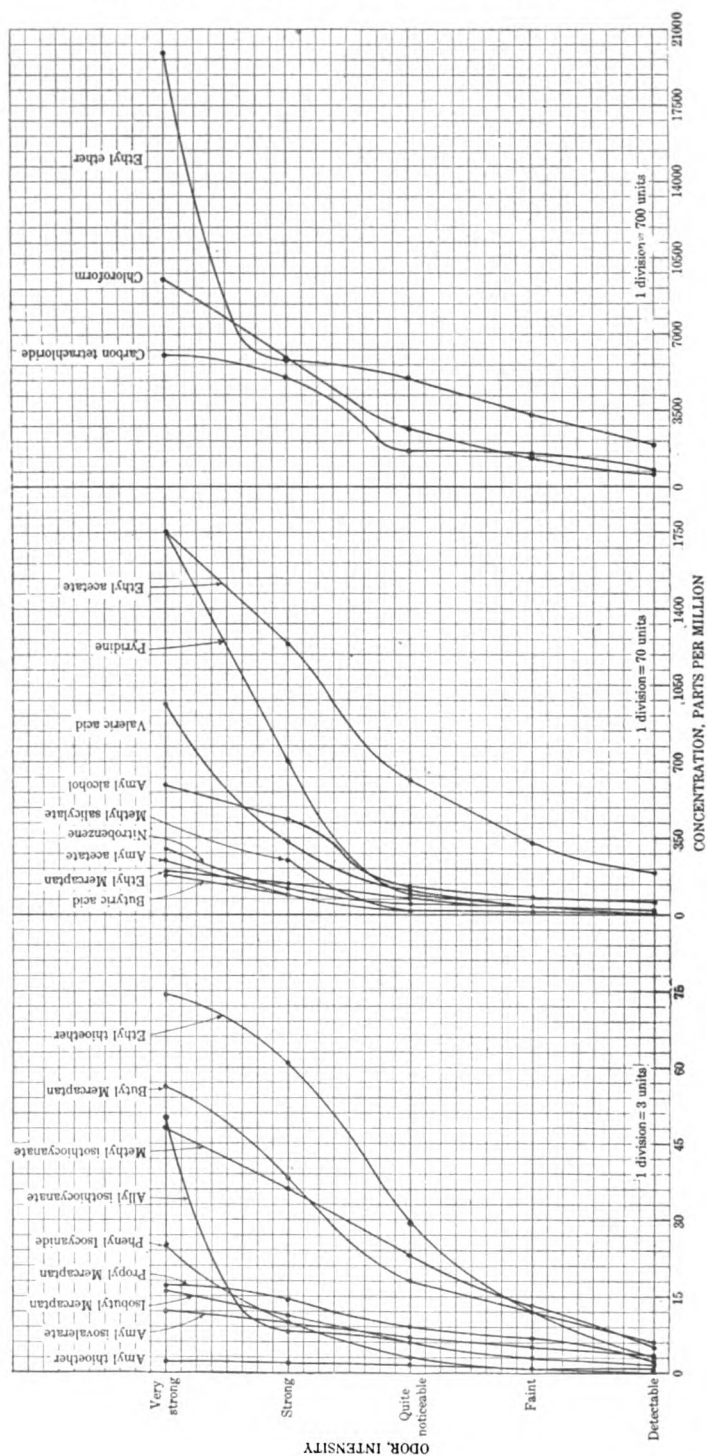


FIGURE 2.—Curves showing concentration of odors for different intensities.

TABLE 3.—*Prices of stenchcs quoted by dealers in chemical supplies.*

Stench.	Eastman Kodak Co.				Eimer & Amend.				Mallinckrodt Chemical Works.			
	Description or designation.	Unit.	Price.	Date of quotation.	Description or designation.	Unit.	Price.	Date of quotation.	Description or designation.	Unit.	Price.	Date of quotation.
Allyl isothiocyanate.....					Artificial mus-tard oil.	Pound.	\$2.50	Apr. 1, 1913				
Amyl acetate.....									{Technical..... Pure..... Technical fu- sel oil. Purified.....	Gallon. Pound. Gallon. Pound.	\$5.00 Do. 7.00 1.25	Oct. 1, 1919 Do. Do. Do.
Amyl alcohol.....	Tertiary C. P.	Kilogram.....	\$12.00	Jan. 1, 1919	Iso, C. P.....	Pound.	.75	Apr. 1, 1913				
Amyl isovalerate.....					Amyl valer-i-anate.	do.....	2.50	do.....				
Amyl thioether.....					Artificial.	Ounce	.60	Apr. 1, 1913				
Artificial musk.....												
Butyl mercaptan.....	n-Butyl mer-captan.	100 grams.....	3.60	Mar. 1, 1919								
Butyric acid.....	Normal C. P.	$\frac{1}{4}$ kilogram.....	11.20	Jan. 1, 1919								
Carbon tetrachloride.....	Technical.....	do.....	1.50	do.....					{Technical..... Pure, redis- tilled, U. S. P. U. S. P. VIII. concentrated.	Pound. do..... do..... Pound.	.22 Do. Do. .46	Oct. 1, 1919 Do. Do. Do.
Chloroform.....	do.....	do.....	2.25	do.....					Technical.....	do.....	1.80	Apr. 5, 1919
Ethyl acetate.....	do.....	do.....	.90	do.....					U. S. P.....	Pound	6.90	Oct. 1, 1919
Ethyl ether.....												
Ethyl mercaptan.....						10 grams	.75	Apr. 1, 1913.				
Ethyl thioether ¹												
Iodoform.....												
Isobutyl mercaptan ¹												
Methyl isothiocyanate ¹												
Methyl salicylate ²												
Nitrobenzene.....												
Oil of peppermint.....												
Phenyl isocyanide ¹												
Propyl mercaptan ¹												
Pyridine ²	C. P.....	Kilogram.....	16.00	Jan. 1, 1919								
Valeric acid.....	Normal, C. P.	350 grams.....	15.10	do.....								

¹ Not found in the market Oct. 15, 1919.² Oil of wintergreen.³ Quotation from Chem. and Met. Eng.

TABLE 3.—*Prices of stenchcs quoted by dealers in chemical supplies—Continued.*

Stench.	Powers-Weightman-Rosengarten Co.				Scientific Materials Co.				Oil, Paint, and Drug Reporter, wholesale market quotations.			
	Description or designation.	Unit.	Price.	Date of quotation.	Description or designation.	Unit.	Price.	Date of quotation.	Description or designation.	Unit.	Price.	Date of quotation.
Allyl isothiocyanate.					Artificially sulfo- cyanide.	Ounce.	\$2.75	Jan. 1, 1919	Mustard oil, artificial.	Pound.	\$12.50	Sept. 29, 1919
Amyl acetate.	(Technical.	Gallon.	\$5.70	Apr. 1, 1919	Technical.	Pound.	1.30	do.	Banana oil.	Gallon.	2.25	Do.
Amyl alcohol.									Amyl acetate.	do.	3.70	Do.
Amyl isovalerate.	Amyl valerate		(¹)	Apr. 1, 1919				Jan. 1, 1919	Fusel oil, crude.	do.	2.50	Do.
Amyl thioether ² .									Fusel oil, re- fined.	do.	4.00	Do.
Artificial musk.									Synthetic.	Pound.	25.00	Do.
Butyl mercaptan.	90 per cent.		(¹)	Jan. 1, 1919	Technical, ab- solute.	Pound.	4.80	Jan. 1, 1919	Technical, 60 per cent.	Pound.	1.55	Do.
Butyric acid.					Technical.	do.	.60	do.	Industrial.	do.	.12	Do.
Carbon tetrachloride.	(Technical.	Pound.	.21	Apr. 1, 1919	C. P.	do.	1.00	do.	U. S. P.	Pound.	.81	Do.
Chloroform.	Technical.	Pound.	.61	Apr. 1, 1919	U. S. P.	do.	1.55	do.	Commercial.	Gallon.	1.00	Do.
Ethyl acetate.	90 per cent.	do.	.75	do.	Abs., C. P.	do.	1.80	do.				
	U. S. P.	do.	1.10	do.			2.75	do.				
	98 $\frac{1}{2}$ per cent.	do.	1.15	do.								
Ethyl ether.	U. S. P., con- centrated.	do.	.49	do.	U. S. P., con- centrated.	Pound.	.80	Jan. 1, 1919	U. S. P., con- centrated.	Pound.	.19	Do.
Ethyl mercaptan.												
Ethyl thioether ² .												
Iodoform.	U. S. P.	Pound.	6.55	Apr. 1, 1919	Crystalline.	Pound.	7.75	Jan. 1, 1919	Pharmaceutical	Pound.	5.30	Do.
Isobutyl mercaptan ² .												
Methyl isothiocyanate ² .	Synthetic.	Pound.	.78	Apr. 1, 1919	Synthetic.	Pound.	1.75	Jan. 1, 1919	U. S. P.	Pound.	.60	Do.
Methyl salicylate ³ .					Rectified.	do.	.65	do.	Myrbane oil, refined.	do.	.15	Do.
Nitrobenzene.					do.		(¹)	do.	Rectified.	do.	8.50	Do.
Oil of peppermint.												
Phenyl isocyanide ² .												
Propyl mercaptan ² .					Medicinal.	Pound.	4.75	Jan. 1, 1919	(¹)	Gallon.	2.50	Sept. 15, 1919
Pyridine ⁴ .					Trihydrated.	Ounce.	2.15	do.				
Valeric acid.												

¹ Listed without price.² Not found in the market Oct. 15, 1919.³ Oil of wintergreen.⁴ Quotation from Chem. and Met. Eng.

COSTS OF STENCHES IN THE MARKET.

Table 3 gives the published quotations of prices of chemicals for stench by five different dealers, and also wholesale market quotations as published by the Oil, Paint and Drug Reporter. The prices therein are not intended to be used for determining relative charges by the different dealers. In fact, such comparisons can not be drawn, because the quotations are of different dates and the materials may not be uniform in quality. The prices quoted by the dealers apply to smaller quantities for retail. For wholesale quantities price quotations of the order given by the Oil, Paint and Drug Reporter can be obtained.

Table 3 also gives descriptions or designations of the different chemicals and the date of each quotation. Although the prices listed are useful for purposes of comparison, they have not much value in determining the cost of adding stench to a gas, as some of the best stenches are not on the market and must be made for the purpose. As a crude product is satisfactory, gas companies can manufacture stench very cheaply.

USE OF STRONG ODOR IN GAS LINES.

In stench concentrations that produce strong odors in gas lines are recommended, because if a stench is to fulfill its purpose the odor must be detectable after the gas has been diluted with air. The greater the concentration of the stench in the gas, the greater is the allowable dilution. The dilution which the concentrations for strong odors will permit before reaching the detectable degree differs according to the stench.

The conclusion should not be drawn that dilution to concentrations below those reported as detectable in Table 2 will make a stench undiscernible. The listed concentrations are for quick detection by a single inhalation of a stream issuing from a funnel, and they exclude the cumulative effects of repeated inhalations. The cumulative effect of some stenches will produce discernible odors from dilutions far below those reported. Experience in warfare has shown that butyl mercaptan, in the open air, at a concentration of 1 part in 10,000,000 parts becomes detectable and even stronger after a few inhalations, whereas under the conditions of the laboratory experiments a concentration of 6 parts in 1,000,000 parts, which is sixty times greater, is reported as detectable.

Other reasons for the use of a strong odor are the following: Some of the stench may be removed from the gas by drip liquor in the mains, and the surface of the pipe may absorb some of it. Fluids in gas meters would do likewise. Small amounts of stench may be removed continuously by drip liquor, but the surface of the pipe will

absorb the odor only when the pipe is freshly exposed to the stench; after the surface is saturated no more stench will be absorbed. If the odor decreases, the surface, acting as a regulator, will evolve stench, and when it increases will again absorb it. Surface absorption may cause delay at first in the transmission of stench, and therefore attempts to locate leaks with newly introduced stench may fail. Several hours should be allowed for the saturation of the surface of long pipes. As the earth is an excellent absorbent for odors, gas leaking from buried pipes must impregnate the earth through which it passes before the odors will be carried with it to the outside air. A delay of several days, according to the size of the leak and the thickness of the earth layer, may thus be caused before the stench becomes noticeable.

A strong odor lessens the danger incurred by any loss of stench in drip liquor and saturates more quickly the pipe surface or the earth surrounding leaks.

QUANTITIES OF STENCHES TO BE USED FOR IMPREGNATING GAS.

Data for the application of stenches to gas lines and the cost of such application appear in Table 4. The two cheapest stenches for imparting a strong odor to 1,000 cubic feet of gas, as shown by the table, are amyl acetate, which costs \$0.0095, and nitrobenzene, which costs \$0.0053. Neither of these chemicals has been termed desirable, because the odors are rather pleasant, and it is believed that disagreeable odors will be most effective for the purpose in view. The odor of amyl acetate is considered very disagreeable by some persons, whereas others like it. Compared with nitrobenzene, amyl acetate offers the best possibilities as a stench. Of the remaining stenches only ethyl mercaptan and pyridine, both of which have extremely disagreeable odors, are quoted at prices that seem at all worthy of consideration for purchases through ordinary commercial channels. Ethyl mercaptan for a strong odor will cost \$0.040 per thousand cubic feet, and pyridine, \$0.043. Ethyl mercaptan contains sulphur, but pyridine does not. Pyridine also has the largest dilution ratio, 71, of the stenches, a factor which makes it especially serviceable. Although pure pyridine at \$2.50 per gallon may be considered expensive, the impure product obtained from the acid washings of light oil should be available at a very much lower price and would serve the purpose admirably.

TABLE 4.—Data for application of stench to gas lines with costs.

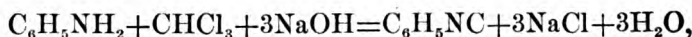
Stench.	Stench required to impart a strong odor to 1,000 cubic feet of gas.			Ratio (quantity for strong odor ÷ quantity for detectable odor).	Stench required to impart a detectable odor to 1,000 cubic feet of gas.			Basic cost of stench.		Sulphur in stench.	Volume of gas given a strong odor per unit of stench. Cubic feet ÷ 1,000.	
	Weight (grams).	Volume (cu. cm.).	Cost (dollars).		Weight (grams).	Volume (cu. cm.).	Cost (dollars).	Unit.	Dollars.			
Allyl isothiocyanate.....	0.9	0.9	0.025	4.5	0.2	0.005	Pound..	12.50	Present.		1 pound.	1 gallon.
Amyl acetate.....	14	16	.0095	13	1.1	1.26	Gallon..	2.25	Absent.		504	4,260
Amyl alcohol.....	45	61	.0644	7	6.4	7.84	do.....	4.00	do.....		32.4	237
Amyl isovalerate ¹	2	2.3		5	4	.47	do.....		do.....		10.9	62.1
Amyl thioether ¹	.4	.4		10	.04	.04	do.....		do.....		227	1,650
Artificial musk.....	3	3.5	.108	6	.001	.000062	Pound..	28.00	Present.		1,350	9,460
Butyl mercaptan ¹	9	9.4		15	.5	.58	100 grams.	3.60	Present.		454,000	
Butyric acid.....	886	559	.095	15	.6	.62	Pound..	4.80	Absent.		151	1,081
Carbon tetrachloride ³	816	544	.56	8.8	128	81	do.....	.12	do.....		50.4	403
Chloroform ³	126	140	.32	6.5	93	62	do.....	.31	do.....		.512	6.77
Ethyl acetate.....	500	696	.21	3	19.4	21.6	do.....	1.15	do.....		.556	6.83
Ethyl ether.....	10	12	.040	7.7	165.1	230	do.....	1.19	do.....		3.60	27
Ethyl mercaptan ¹	6	7		20	1.3	1.55	do.....	1.80	Present.		.908	5.44
Ethyl thioether ¹	1	1.2		5	.3	.36	do.....		do.....		45.4	315
Iodoform.....	3	3.6	.057	15	.5	.58	Pound..	5.30	Absent.		75.7	541
Isobutyl mercaptan ¹	43	36	.053	15	.2	.23	do.....		do.....		908	
Methyl isothiocyanate ¹	16	13	.18	4	.4	.47	Pound..	.60	Present.		454	3,150
Methyl salicylate.....	9.5	10.4		14	2.8	3.3	do.....	.15	Absent.		151	1,250
Nitrobenzene.....	1	1.4		17	4	3.3	do.....	8.50	do.....		10.6	105
Oil of peppermint.....	64	65	.043	71	.68	.716	do.....		do.....		28.4	391
Phenyl isocyanide ¹	39	41	1.37	49	.06	.061	do.....		do.....		47.8	364
Propyl mercaptan ¹					.2	.24	do.....		Absent.		454	3,785
Pyridine.....					.9	.91	Gallon..	2.50	Present.		378	2,700
Valeric acid.....					.8	.85	Pound..	16.00	do.....		7.10	58.2
											11.6	92.3

¹ Not found in the market.² Maximum concentration under conditions of experiment, which was only of detectable intensity.³ Should not be used in fuel or illuminating gas.

Amyl thioether and phenyl isocyanide both have very disagreeable odors, are powerful in very low concentrations, and have dilution ratios of 10 and 17, respectively. Thus they are well suited for use in gas lines. They are not listed commercially, are not difficult to produce, and manufacturers of chemicals would undoubtedly supply them if a sufficient demand were created. As only very low concentrations are required, they should prove particularly well adapted for use as stenchers. Amyl thioether contains sulphur; phenyl isocyanide contains none. To assist chemists at gas works to produce phenyl isocyanide or amyl thioether, directions are given here. Hofmann⁴ describes the preparation of phenyl isocyanide as follows:

Aniline, chloroform, and alcoholic potassium hydroxide are mixed together and distilled, yielding a malodorous liquid. On distilling this product, alcohol and water first separate, after which an oil containing aniline is evolved. Oxalic acid added to the oil precipitates the aniline as oxalate. Water is removed from the remaining oil with potassium hydroxide. Distillation of the residue yields the pure product, which is green in transmitted and blue in reflected light. This liquid boils at 167°, but is subject to change, probably polymerization, with rise of temperature to 230° C. According to Richter,⁵ distillation at reduced pressure prevents this change.

Hofmann does not mention the quantities used or the yields. Although his directions for preparing the pure phenyl isocyanide are specified, the product need not be pure for use as a stench. The impure product could be used by mixing the aniline and chloroform in molecular proportions according to the reaction,



with a 25 per cent solution of caustic soda one-fourth in excess of the molecular proportion, and by boiling the mixture under a reflux condenser for one hour. Such a product could be prepared at a gas house. Figuring on a yield of only 50 per cent of phenyl isocyanide, the cost of the stench would not be more than \$0.006 or \$0.007 per 1,000 cubic feet of gas.

The preparation of amyl thioether is described by Beckmann⁶ as follows:

"Isoamyl alcohol was treated with phosphorous pentachloride to form the amyl chloride, which was purified. This was treated with a little more than the required quantity of potassium sulphide in alcohol (made by saturating half of a solution of alcoholic potas-

⁴ Hofmann, A. W., Ueber eine neue Reihe von Homologen der Cyanwasser-stoffsaure; *Ann. Chem.*, vol. 144, 1867, pp. 114-120.

⁵ Richter, V. von, *Organic chemistry or chemistry of the carbon compounds*; 1st English ed., translated by P. E. Spielmann; Philadelphia, 1916.

⁶ Beckmann, E. O., Ueber die Oxydations-produkte der Dialkylsulfide und ahnlicher Verbindungen; *Jour. Prakt. Chem.*, vol. 17, 1878, pp. 440-441.

sium hydroxide with hydrogen sulphide and adding the other half). After heating the mixture in a closed vessel in a water bath for 10 hours, it was distilled. The amyl thioether all came over at 213° to 214° C. If unpurified amyl thioether were made by chemists at the plant, gas could be impregnated with it to a strong odor at a cost of about \$0.01 per 1,000 cubic feet."

Table 4 shows that artificial musk, having the high price of \$28 a pound, gives a detectable concentration at the lowest cost. It is solid and comparatively nonvolatile, so that concentrations with higher intensities of odors were not obtained by passing air through the granular material at room temperature. For that reason, and also because the odor is pleasing and common, the use of musk as a warning is not feasible.

On account of their low odor intensities and the resulting high cost, chloroform and carbon tetrachloride would hardly be used. Moreover, these chemicals would be dangerous, as well as expensive, for use as warning odors, because in contact with flame they may generate phosgene, which is intensely poisonous. The amount of chloroform that may be left in the unpurified mixture of phenyl isocyanide is too small to warrant its separation for hygienic reasons.

Until there is a large decrease in prices most of the other stench can not be considered for the purpose of imparting odor to gas, except possibly the mercaptans. Butyl and ethyl mercaptan, which were made experimentally on a large scale for gas warfare, are particularly disagreeable in odor at very low concentrations.

METHODS FOR IMPREGNATION.

The amount of liquid stench needed for a city depends on the quantity of gas used. An average city of 100,000 population with coal or water gas supply will not usually exceed 3,000,000 cubic feet maximum daily consumption. To impart a strong odor to this gas would require only 12.7 gallons of amyl acetate, 0.32 gallon of pure amyl thioether, 9.5 gallons of ethyl mercaptan, 0.79 gallon of pure phenyl isocyanide, or 52 gallons of pyridine. Any device that will deliver the liquid stench at a constant and controllable rate to a gas stream, where it will be volatilized as introduced, can serve as an impregnator.

Gravity feed with control by means of a needle valve and sight glass can be arranged very simply. The disadvantage of gravity feed is the constant supervision required to maintain uniform delivery, but such feed will probably be satisfactory enough for the needs of gas impregnation. Mechanical devices are the most dependable as regards uniformity of delivery; the automatic lubricator, model T, made by the Richardson, Phoenix Co., of Milwaukee, Wis.,

is well adapted for the purpose. A one-tenth horsepower motor will drive the apparatus at constant speed and so maintain uniform delivery of the liquid stench. The rate of delivery can be varied by means of a series of motor-driven step pulleys that turn a crank connecting with a reciprocating ratchet lever, of variable length, on the lubricator. As the length of the lever increases, the volume of liquid delivered decreases. Such an arrangement of motor, step pulleys, and lever would give complete control of the delivery. The cost of the necessary machine is about \$200. If the gas is compressed for delivery, the injector could regulate the rate of delivery of stench by the action of the compressor. This method will secure absolute uniformity of impregnation.

Volatilization of liquid may be produced by simply allowing the warm gas as generated and cleaned to pass over the liquid while the stench is being delivered into a long horizontal pipe with upturns at each end. Two cocks should be placed in the underside of the pipe to allow liquid to be drained out or residuum to be washed out when necessary.

A simpler method, which should prove reliable enough, is to measure the required quantity of liquid stench for each interval of time, for example, four or eight hours, and pour it into a long, horizontal pipe, like that described above, through a funnel and small pipe with a valve inserted. The liquid would soon be evaporated, but the natural mixing of the gas in the gasometer would produce an even mixture of gas and stench before delivery to the mains.

A stench that is allowed to enter the gasometer must necessarily be not more than slightly soluble in water; otherwise the water seals would tend to remove a considerable quantity of stench from the gas, and, aside from the loss of the stench, the danger would arise of creating a nuisance in the vicinity, as highly polluted water releases the stench when exposed to the air. With the possible exception of pyridine, the stenches listed as desirable are sufficiently insoluble in water that no nuisance would arise. The odor of pyridine could escape from the gasometer because of the solubility of pyridine in water; nevertheless, it is believed that with concentrations of low percentage in the gas, the travel of the stench to the air outside would be too slow to become offensive.

SULPHUR IN STENCHES.

Many classes of organic sulphur compounds have a disagreeable and powerful odor. Some of the best stenches belong to this group. Because the gas manufacturer endeavors to reduce the sulphur content of gas, the addition of sulphur in the form of stench is not altogether desirable. The quantity of sulphur in the added stench,

however, is not large as compared to the normal amount in city gas. Table 5 gives the amounts of sulphur in different sulphur stenchers needed to impart a strong odor to gas.

TABLE 5.—*Amounts of sulphur in the sulphur-bearing stenchers as used to impart a strong odor to gas.*

Stench.	Weight of stench for strong odor in 1,000 cubic feet of gas.	Weight of sulphur in the stench per 100 cubic feet of gas.	
		Grams.	Grains.
Allyl isothiocyanate.....	0.9	0.029	0.45
Amyl thioether.....	10.0	.18	2.8
Butyl mercaptan.....	3.0	.11	1.7
Ethyl mercaptan.....	10.0	.52	8.0
Ethyl thioether.....	6.0	.21	3.2
Isobutyl mercaptan.....	1.0	.036	.56
Methyl isothiocyanate.....	3.0	.13	2.0
Propyl mercaptan.....	1.2	.051	.79

The table shows that allyl isothiocyanate would add 0.45 grain of sulphur per 100 cubic feet of gas in strong odor concentrations, which is the minimum figure. The maximum is 8.0 grains of sulphur per 100 cubic feet of gas for ethyl mercaptan. Most city ordinances on sulphur content allow a maximum of 15 grains of sulphur per 100 cubic feet of gas. Thus 8.0 grains of sulphur per 100 from ethyl mercaptan would be 53 per cent of the allowable quantity, while allyl isothiocyanate would introduce only 3 per cent of the sulphur allowable. These figures indicate that it is feasible to use any of the sulphur stenchers.

SUMMARY AND CONCLUSIONS.

The impregnation of natural gas or blue water gas with a stench-imparting chemical provides a means for reducing loss from leakage and for eliminating accidental poisoning and explosions. Measurements of the intensities of odors have been used to ascertain the quantities of stenchers needed to impart a strong odor to gas and to calculate the costs. Use of the strong odor is advised. Stenchers that possess a disagreeable odor serve best as warnings. Of those examined, amyl thioether, ethyl mercaptan, phenyl isocyanide, and pyridine present the best possibilities with regard to the cost of impregnation, as well as to other properties required.

Gas can be uniformly impregnated with a stench by allowing it, when cleaned and still warm, to pass through a horizontal pipe into which stench liquid is delivered at a uniform rate. Gravity feed of the liquid can be used, but requires more supervision than mechanical appliances, such as engine lubricators. The lubricator manufactured by the Richardson Phoenix Co., of Milwaukee, Wis., is well adapted

for gas impregnation. Gas can be impregnated by placing in the pipe at regular intervals a quantity of stench and allowing the natural mixing of gas in the gasometer to make a uniform concentration.

None of the stenches that contain sulphur, if added to gas in amounts to produce strong odors, would carry sufficient sulphur to inhibit commercial use of the gas. The maximum addition of sulphur is 8.0 grains per hundred cubic feet of gas, imparted by ethyl mercaptan.

Savings resulting from the use of stench in gas would probably total more than the costs of the stench.

Suggestions made in this paper should be regarded as tentative, pending tests on a large scale.

